040606 Polymer Properties Final (300 points)

1) When confronted with fluctuations as a response to perturbations as a primary signal it is often useful to consider a Fourier transform of the data to inverse-space and to analyze the data in terms of the amplitudes of response for various modes (modal analysis). We directly used this approach in three topical areas: Cahn-Hilliard linear theory; RPA and in developing the Rouse model. The approach is also used directly in spectroscopy and scattering as the basis of FTIR, FTNMR and XRD/scattering. It is further commonly used to analyze many types of computer simulations.

a) Explain what a fluctuation is, giving examples from linear Cahn-Hilliard theory; the RPA analysis; and from the Rouse model. (You will need to consider fluctuations of composition in time, space and fluctuations in position with time. Include how fluctuations are related to temperature including the behavior at absolute 0, as well as the modulation of fluctuations by transport properties such as the diffusion coefficient or mobility. Also mention the importance of an assumption of incompressibility and the importance of the free energy curve.)

b) Describe how the concept of fluctuations can be used to describe the response of a system to a free energy curve such as the free energy of mixing described by the Flory-Huggins equation. (Plot free energy change versus composition above, below and at the critical temperature; show how fluctuations in composition can describe the system response in all of the major regimes of these curves.)

c) Often a primary mode or primary modes are desired in a modal analysis. At times the inverse-space distribution of modes is of interest. Describe (compare and contrast) the application of modes in linear Cahn-Hilliard theory, the RPA and in the Rouse model. Indicate if a single mode or a distribution of modes are of primary interest.

d) In FTIR the absorption of IR radiation is measured as a function of wavelength (interference position) using a Michaelson-interferometer. The raw signal represents fluctuations associated with the amplitude of energy in the material for different wavelengths. Explain, in the context of parts a to c, how a Fourier transform could be used to analyze this data. Is a single mode or a spectrum of modes desired from such an analysis? (This is a tricky question, consider only one absorption band.)

e) Explain how a modal analysis might be of use in analyzing a computer simulation that resulted in the distribution of persistence unit velocities for a polymer chain as a function of spatial position. (What is desired from such a dynamic simulation?)

2) The Hydrodynamic radius is used to describe both regular objects such as a sphere and fractal objects such as a polymer coil.

a) What is the hydrodynamic radius of a sphere?

b) If Stokes law is used to calculate the hydrodynamic radius of a polymer coil, is the coil considered draining or non-draining? Explain.
If the Rouse model is used to calculate the hydrodynamic radius of a polymer coil is it considered draining or non-draining? Explain.

c) In part "b", which of these sizes would be larger? Why?

d) The hydrodynamic radius can be measured using dynamic light-scattering. Explain how this measurement could give the size of suspended particles undergoing Brownian motion.

e) Why might a plot of $1/\tau$ be proportional to q^2 in a DLS measurement? (Define q in terms of size and use the relationship between distance traveled (size) and time for Brownian motion.)

3) An expression for the free energy of an isolated chain in a theta or in a good solvent can be obtained from the Flory Krigbaum approach and the Boltzmann principle.

a) Give the expressions for the free energy of these two cases showing how the expressions relate to the conformational probability functions discussed in class.

b) We also discussed a "new" thermodynamics where size-scale dependence to the entropy can lead to unexpected thermodynamic accommodations for long chain molecules. Use this concept to explain how a polymer chain in a very good solvent responds to a reduction in temperature through the theta temperature to the collapsed state. (First describe with a sketch the very good solvent condition. Then describe local chain contraction following the blob model. Next describe the rapid approach to theta conditions. Finally describe the limit of intra-chain accommodation and the coil/globule transition.)

c) Describe the overlap concentration and give the molecular weight dependence of the overlap concentration. (Make a sketch showing the approach to overlap concentration for a polymer solution.)

d) If one desired the force/elongation behavior of a single chain such as a chain in a swollen elastomer, would the Flory-Huggins expression or the Flory-Krigbaum expression for free energy be more useful? Why?

e) In a non-swollen (dry) elastomer, what complications would you anticipate in the use of the free energy expression you chose in part "d"?